

MIXING SMALL AMOUNTS OF CRUDE OIL WITH LARGE AMOUNTS OF ASPHALTENE PRECIPITANT

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ABSTRACT

The appearance of asphaltenes as a separate phase during mixing depends on local concentrations of asphaltic crude oil and the precipitating agent, usually a paraffinic crude or refined mineral oil. The order of mixing accounts for differences that are observed when crude oil is initially the minor component compared to mixing a small amount of precipitant with larger amounts of asphaltic crude oil and equilibration may be very slow, increasing the impact of kinetic effects.

If asphaltenes form quickly at boundaries of contact between crude and precipitant, mixing can be significantly retarded. A persistent metastable condition can be established. This retardation of mixing of two otherwise miscible fluids has implications for wettability alteration and flow through porous media. In this paper we demonstrate the effect of asphaltene precipitation on mixing and the consequences with respect to laboratory core tests that involve direct displacement of crude oil by refined oil.

INTRODUCTION

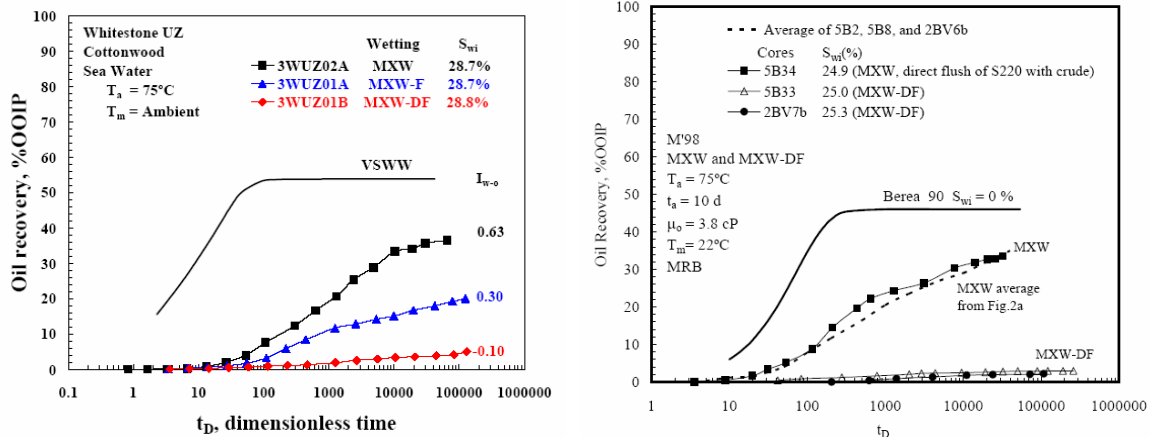
Some of the heaviest, most polar components of crude oils, usually referred to as asphaltenes, are insoluble in normal alkanes. We have reported previously on observations of the least soluble asphaltenes, those that appear at the onset of asphaltene precipitation (Buckley et al., 2006). The amount of asphaltene that forms as the solvent conditions worsen has also been reported (Akbarzadeh et al., 2004; Wang and Buckley, 2005). Wetting alteration to less water-wet or even oil-wet conditions has been demonstrated in sandstone and carbonate cores when crude oil is displaced with a paraffinic mineral oil such as Soltrol 220 (Tie et al., 2003; Tong and Morrow, 2004; Tie and Morrow, 2005) or by some of the base oils used to make up synthetic oil-based drilling fluids (Zhang et al., 2005).

As an oil becomes a poorer solvent for its asphaltenes, it reaches the point where asphaltene flocs first become visible, often referred to as the onset condition. Further reductions in solvent quality lead to formation of additional asphaltene flocs and their

size increases. Kinetics of the precipitation process are slowest near the onset and much more rapid as solvent quality decreases (Yudin et al., 1998; Mason and Lin, 2003).

Buckley et al. (1998) proposed several mechanisms by which oil components, including asphaltenes, can interact with silicate surfaces to alter wetting. Asphaltenes and other polar components can adsorb through various ionic interactions that are influenced by surface charge and the presence of water and dissolved salts. In addition, asphaltenes can adsorb to a greater or lesser extent if their state of solvation changes. Al-Maamari and Buckley (2003) showed that water-advancing contact angles reached a maximum value near the onset of asphaltene precipitation for many crude oils, a process referred to as surface precipitation, which may precede bulk precipitation. Surface precipitation near the onset is envisioned as analogous to the growth of two-dimensional structures at slightly better dispersal conditions than those required to create three-dimensional flocs in bulk, which has been demonstrated for colloidal systems (Picard, 1997). Either surface or bulk precipitation can make surfaces more oil-wet.

Exposure to crude oil in the presence of connate brine can render a core mixed-wet (MXW) (Morrow, 1990). The altered wetting condition persists when the crude oil is displaced to leave a film of oil components on altered surfaces (MXW-F). Because of the still more oil-wet conditions that can result, cores in which an asphaltic crude oil is displaced by an asphaltene precipitant have been designated as MXW-DF (mixed-wet-direct flood), to distinguish them from cores in which MXW-F conditions have been established by miscible displacement of crude oil by decalin or another asphaltene solvent. Rates of spontaneous imbibition of water for all three conditions are shown in Fig. 1a for a limestone core (Tie, et al., 2005); MXW and MXW-DF imbibition rates are shown in Fig. 1b for Berea sandstone (from Tong and Morrow, 2006). Imbibition rates are scaled to a dimensionless time to account for differences in core geometry, permeability, porosity, interfacial tension, and fluid viscosities (Ma et al., 1997).



(a) MXW, MXW-F, and MXW-DF states in limestone (after Tie et al., 2005)

(b) MXW and MXW-DF states in sandstone (after Tong and Morrow, 2006)

Figure 1. The effect of exposure to oil and different oil displacement conditions on the rate of spontaneous imbibition of water indicates changes in wetting in porous media. MXW conditions are generally the most water-wet whereas, for asphaltic oils, MXW-DF conditions are the least water-wet.

While it is clear that asphaltene precipitation is involved in rendering the MXW-DF cores more oil-wet than they would be if crude were displaced with decalin, the mechanism of wetting alteration remains to be clarified. Tong and Morrow (2006) measured imbibition rates for a sequence of wetting conditions in a Berea sandstone core. Initially the core was aged at S_{wi} in Minnelusa crude oil. Figure 2 shows rates of imbibition after each of a series of six displacements. Crude oil was displaced initially by Soltrol 220 (S220), an asphaltene precipitant, creating MXW-DF conditions in this core. Cycles 1 and 2 show almost no imbibition of water. In the third and fifth cycles, the displacing fluids were asphaltene solvents, toluene and α -methyl-naphthalene (AMN), respectively. Imbibition rates and oil recoveries increase dramatically in these cycles. Cycles 4 and 6, with S220, show rates of imbibition that are higher than the initial MXW-DF conditions, but are less water-wet than the cycles with asphaltene solvents. If there is no additional contact with crude oil, it is not clear why less water-wet conditions should be observed in the S220 cycles 4 and 6. One suggestion is that adsorbed components act as more water-wet surfaces in toluene and AMN, whereas they appear to be less water-wet to S220. A second possibility is that pockets of crude oil remain in the core, even after many displacements including those with asphaltene solvents and that small amounts of crude oil diffuse into S220 during each cycle, causing additional asphaltene precipitation.

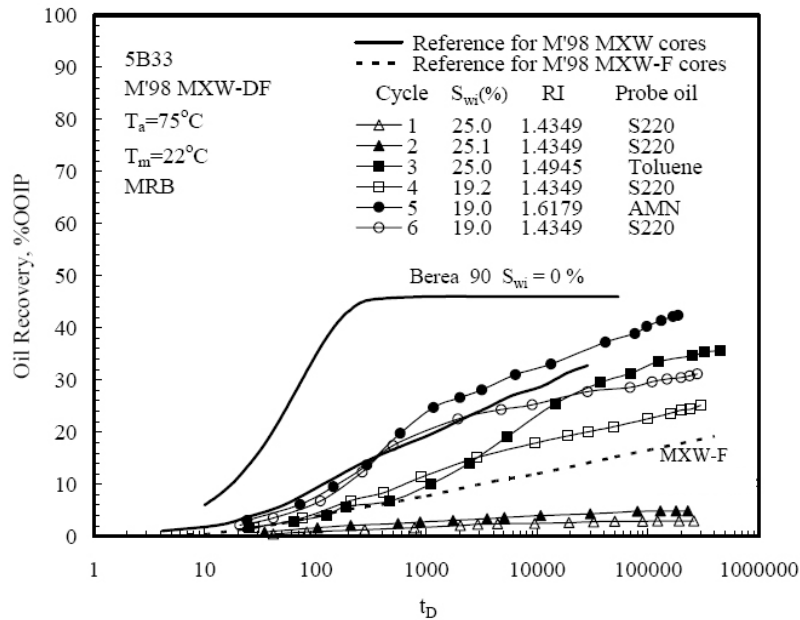


Figure 2. The effects of flooding with asphaltene precipitants and solvents on core wettability (from Tong and Morrow, 2006).

Examination of “compatibility” tests in which a small amount of crude oil is mixed with a larger volume of precipitant such as a paraffinic mineral oil suggest a mechanism by which small pockets of crude oil can be retained in a core when an asphaltic crude oil is displaced by an asphaltene precipitant.

METHODS AND MATERIALS

Fluids

Hydrocarbons tested included n-heptane, n-decane, decalin, toluene, AMN, S220 ($\mu=3.8$ cP), and a high viscosity mineral oil ($\mu=180$ cP). All were used as received. Properties of crude oils are summarized in Table 1. Brine compositions are summarized in Table 2.

Table 1. Crude Oil Properties

Crude Oil	$^\circ\text{API}$	n-C ₇ asphaltenes (wt%)	μ at 20°C (cP)
Cottonwood-03	26.4	2.5	26.1
Gullfaks-96	27.1	0.4	15.8
LB-03	30.6	0.1	13.1
Minnelusa-02	24.3	8.6	60.5
Uwyo-E-04	24.7	2.8	38.5
Uwyo-M-04	21.9	7.0	89.7

Table 2. Brine Compositions

Brine	NaCl (g/L)	KCl (g/L)	CaCl ₂ (g/L)	MgCl ₂ (g/L)	MgSO ₄ (g/L)	Na ₂ SO ₄ (g/L)	NaN ₃ (g/L)	pH	TDS (mg/L)
Minnelusa (MRB)	29.8	-	2.1	-	0.394	5.903	0.1	6.8	38,297
Sea water (SSW)	28	0.935	2.379	5.365	-	-	0.1	6.6	36,779

Compatibility Tests

Compatibility between asphaltenes in a crude oil and a paraffinic solvent is sometimes assessed by mixing a small amount of crude oil with a large volume of a solvent. No standard procedure has been defined for such tests; exact protocols appear to vary from one company to another. For compatible oils, little or no flocculated asphaltene is visible. The crude oil and solvent mix completely. If the oils are incompatible and if crude oil is the denser fluid, drops of crude oil will sink through the solvent without much mixing and settle as a distinct phase at the bottom of the mixing vessel. The larger the volume of the second phase for a given amount of crude oil and solvent, the less compatible the two fluids are deemed to be. Such tests are often used to assess the efficacy of asphaltene dispersant chemicals.

In this study, test tubes, centrifuge tubes, and a pendant drop apparatus (Data Physics OCA20) were used to observe mixtures of crude oils and hydrocarbon solvents and precipitants for qualitative assessments of fluid compatibility.

Core Tests

Tests were conducted using Berea sandstone cores. Core properties are given in Table 3. Cores were vacuum saturated with brine, aged in brine at 75°C for 10 days, then flooded with oil at 45°C to establish initial water saturation, S_{wi} . S_{wi} was established simply by displacement with Minnelusa crude oil for Tests 1 and 2. For Test 3, a comparable value of S_{wi} was established using a viscous mineral oil that was miscibly displaced by decalin, followed by Gullfaks crude oil. Cores were aged in crude oil for 10 days at 75°C. Crude oil was then displaced with S220. The produced oil mixture of crude and S220 was collected, weighed, and the density of the mixture determined.

Table 3. Berea Sandstone Core Properties

Test	Core ID	Length (cm)	Diameter (cm)	Porosity (%)	Permeability (md)	S_{wi} (%)
1	Ev8h33b	7.443	3.774	16.39	74	24.5
2	Ev8h32b	7.450	3.776	16.57	78	26.2
3	Ev8h31b	7.627	3.774	16.58	74	24.0

RESULTS AND DISCUSSION

Compatibility Test Results

An extreme case of incompatibility is shown in Fig. 3. About 10 μL of Minnelusa-02 crude oil were dispensed slowly into about 6.5 mL of n-C₁₀. There was little, if any, mixing between these two oils even after many hours of contact. The interface between them was extremely rigid. Other oils with lower asphaltene contents showed less extreme evidence of incompatibility, spreading in a pancake on the bottom of the quartz glass observation cell. Those with the fewest asphaltenes mixed slowly with n-C₁₀, as indicated by a gradient of coloration in the hydrocarbon phase. Less rigidity and more rapid mixing occurred when the hydrocarbon was decalin. Replacement of n-C₁₀ by toluene or mixing toluene into n-C₁₀ resulted in rapid dissolution of Minnelusa-02 oil. Results are summarized in Table 4.



Figure 3. Minnelusa-02 crude oil metered slowly into n-decane forms rigid structures and does not mix. The rectangular feature at the top is a needle with OD of 1.07 mm and ID of 0.70 mm.

Table 4. Compatibility Test Results

Oil	Hydrocarbon	Precipitant?	Mixing	Appearance
Cottonwood-03	n-C ₁₀	yes	slow	initially slightly rigid; after 17 hr, rigid films appear to be preventing further mixing
Gullfaks	n-C ₁₀	yes	slow	not rigid, oil spreads on the bottom of the cell
LB-03	n-C ₁₀	yes	slow	not rigid, oil spreads on the bottom of the cell
Uwyo-E-04	n-C ₁₀	yes	slow	slightly rigid
Uwyo-E-04	decalin	no	slow	slightly rigid
Uwyo-M-04	n-C ₁₀	yes	none	rigid
Uwyo-M-04	decalin	?	slow	less rigid
Minnelusa-02	n-C ₇	yes	none	very rigid
Minnelusa-02	n-C ₁₀	yes	none	very rigid
Minnelusa-02	decalin	?	slow	less rigid
Minnelusa	n-C ₁₀ /toluene ^a	yes/no	fast	

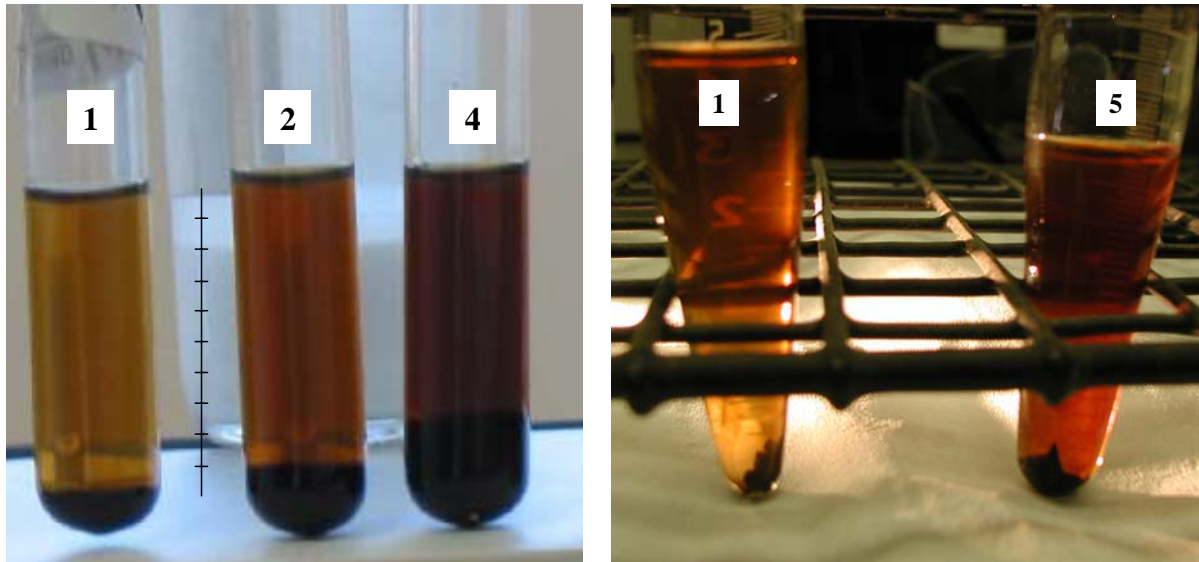
Minnelusa	n-C ₁₀ +toluene ^b	no	fast	obvious coloration of hydrocarbon phase
Paraffin oil	n-C ₁₀	n/a	slow	

^a n-C₁₀ followed by toluene (after removal of n-C₁₀)

^b mixture of n-C₁₀ and toluene (approximately 50:50 n-C₁₀:toluene)

The results of these compatibility tests correlate principally with the amount of asphaltene and secondarily with viscosity difference between the fluids. Cases identified by de Boer et al. (1995), as likely to cause asphaltene damage typically have small amounts of unstable asphaltenes. These oils would not be identified by this test.

Figure 4 shows the results of two additional experiments with Minnelusa crude oils. In Fig. 4a, drops of crude oil were added to S220. A scale has been added to the picture to allow estimation of the fraction of the volume that is in the crude oil phase. If the rounded bottom of the test tube is ignored, approximately 10% of the liquid volume in the center tube is in the denser phase, a surprising observation since only two drops of crude oil (~0.02 mL) were added to 3 mL of S220, giving a crude oil concentration of less than 1%. Judging by the color of the S220 phase, some crude oil mixes into the S220 and the volumes indicate that there is a significant amount of S220 in the denser phase as well, but any further mixing is very slow. When that mixing process is accelerated by vigorous ultrasonic agitation, the result is a small amount of powdery asphaltenes and a well-mixed liquid phase as shown in Fig. 4b. It appears that asphaltene formation at the boundary between crude oil and hydrocarbon precipitant can slow the mixing process. The extent to which mixing is restricted varies with the amount of asphaltene in the oil and the kinetics of asphaltene precipitation which can be very fast when the concentration of non-solvent is high.



(a) Mixtures with 3mL S220 that were not agitated.

(b) Mixtures with 3-5 mL S220 that were agitated in an ultrasonic water bath for ~20 min, followed by centrifugation.

Figure 4. Mixtures of Minnelusa crude oil with Soltrol 220. The labels indicate the number of drops of crude oil—added one drop at a time—to Soltrol 220. Each drop has a volume of approximately 0.01 mL.

Core Tests

When an asphaltic crude oil is displaced from a core by an asphaltene precipitant such as S220, there will be a mixing zone where the concentration of non-solvent is high and asphaltenes precipitate rapidly. One effect of this incompatibility is to depress spontaneous imbibition of water as shown in Figs. 1 and 2 for the MXW-DF conditions. The cyclic tests in Fig. 2 suggest that there may be a reservoir of crude oil with unprecipitated asphaltenes that can continue to alter wetting when the core is repeatedly flooded with S220. To test that possibility, two coreflood tests were conducted with Minnelusa crude oil, the most asphaltic of the oils tested, and an additional test was made with Gullfaks, one of our least asphaltic samples.

Cores were initially saturated with brine, then flooded with crude oil to establish S_{wi} . The densities of the oils at 20°C are summarized in Table 5. From the density and weight of the produced oil, the amount of crude oil produced could be calculated. Figure 5 shows micrographs of the produced fluids. Both contained asphaltenes, but the amount was much greater in the case of Minnelusa than it was for Gullfaks. Test details and results are summarized in Table 6.

Table 5. Fluid Densities at 20°C

Fluid	Density (g/cm ³)
Gulfaks-96	0.8829
Minnelusa-02	0.9080
S220	0.7894

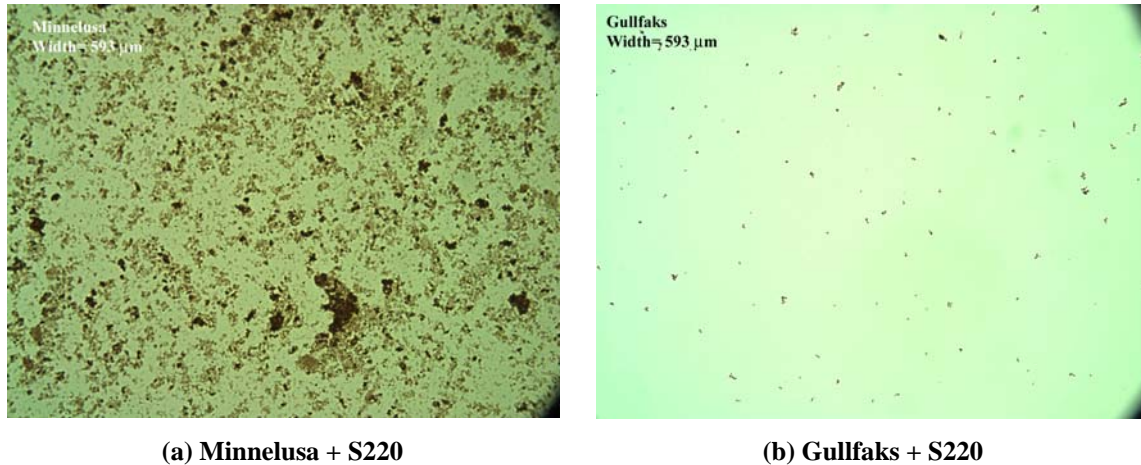


Figure 5. Micrographs of produced oil from MXW-DF experiments shows production of flocculated asphaltenes.

Table 6. Core Flood Test Parameters and Results

Test	Oil	Brine	S220 (PV)	Produced oil (g)	Density (g/cm ³)	Oil remaining (ml)	%OOIP
1	Minnelusa	MRB	7.5	84.138	0.8001	0.81	7.9
2	Minnelusa	MRB	5	75.614	0.8011	0.88	8.6
3	Gulfaks	SSW	5	73.073	0.8004	0.01	0.1

Retention of oil was significant only for the asphaltic Minnelusa sample. There was essentially no retention of Gulfaks. The wettability of the MXW-DF Gulfaks sample can be assessed from the rate of water imbibition in a similarly treated core shown in Fig. 6. The core is less water-wet than the reference very strongly water-wet condition indicated by the solid line, but water imbibes to a much greater extent than for MXW-DF cores prepared with asphaltic oils.

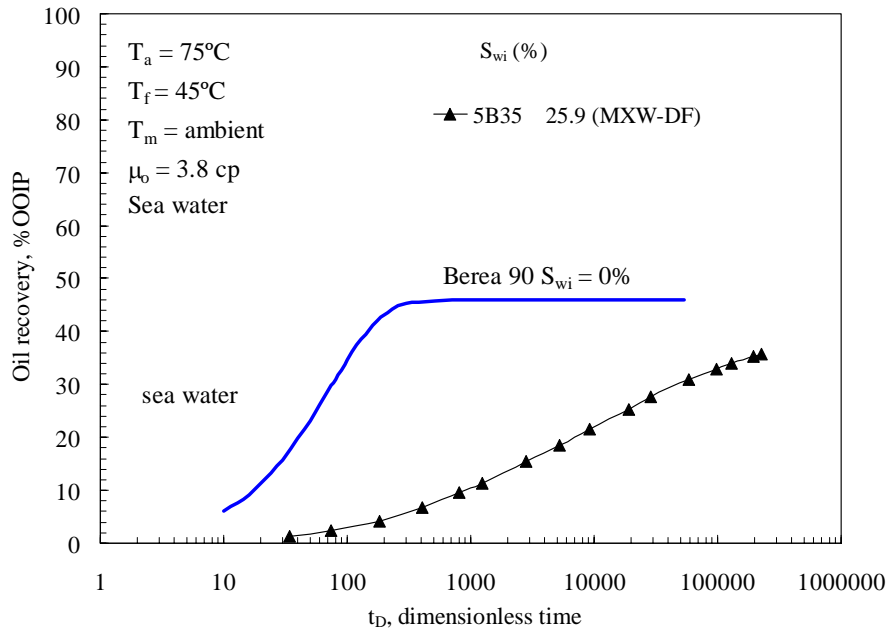


Figure 6. Imbibition of water into a Berea sandstone core aged in Gullfax, with oil displaced by S220 (MXW-DF conditions).

As shown in Table 1, Minnelusa-02 contains 8.6% n-C₇ asphaltenes. Although the amount of asphaltene retained in the cores was not quantified, Fig. 5a shows that much of the precipitated asphaltene was produced from the core.

Additional evidence for retention of oil, as opposed to precipitated asphaltenes, was captured in video recordings of glass micromodel displacements of Moutray crude oil by Soltrol 130, a less viscous paraffinic mineral oil blend (Buckley, 1995). Precipitate collected at zones where color changes indicated contact of Soltrol with crude oil. Precipitated asphaltenes were observed to move with the oil phase when the model was waterflooded.

The inverse situation, direct displacement of S220 by crude oil, produces wetting conditions that are similar to crude oil alone (Tong and Morrow, 2006). There must exist mixing zones with concentrations of non-solvent adequate to precipitate asphaltenes in this case as well. The major difference between these two situations is that at the end of the crude oil flood, small pockets of S220 might exist, but diffusion of small amounts of S220 into a large volume of crude oil will not produce further precipitation, whereas small amounts of trapped crude oil diffusing into a large reservoir of S220 does produce additional asphaltene precipitation.

CONCLUSIONS

- Contact of a small amount of an asphaltic crude oil with a large volume of an asphaltene precipitant can create a mixing zone where asphaltenes precipitate rapidly, forming a skin that limits further mixing of the two fluids. Mixing under these conditions requires input of considerable energy.
- Displacement of an asphaltic oil by an asphaltene precipitant results in much less water-wet and perhaps even oil-wet conditions in either carbonate or sandstone cores. Pockets of crude oil remain trapped in the core. Further asphaltene precipitation and wetting alteration can occur if the core is reflooded with asphaltene precipitants.
- An oil compatibility test based on interactions between a small amount of crude oil and a large amount of precipitant mainly correlate to the amount of asphaltene in the oil. The classic cases of asphaltene damage caused by oils with very small amounts of unstable asphaltenes would not be identified by this test.

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